2E21

物質設計のための二・三次元系用 Generalized Elongation 法の開発

（九大院・総理工[1], JST-CREST[2]）　○青木 百合子[1,2], Gu Feng Long[1],

Introduction:

Early 1990s, Imamura and Aoki developed the elongation method [1-4] in order to efficiently determine electronic structures of random polymers. Their original idea of the elongation method comes from experimental polymerization/copolymerization procedures. Contrast to other approximation methods for large systems, the elongation is fully variational. It is confirmed that the total energies obtained by this method are in excellent agreement to those by the conventional method. The error of the elongation method is within 10^{-9} a.u./atom [5-7]. The elongation method has been applied to various periodic and/or aperiodic quasi-one-dimensional systems [8-10] for the electric and optical properties.

However, the original implementation of the elongation method was restricted only to quasi-one-dimensional systems. It has been questioned whether it is applicable for three-dimensional systems. In this presentation, a generalized elongation method will be presented for any dimensional systems. Some benchmark test calculations are presented to show the reliability and applicability of the generalized elongation method.

Methodology:

Fig. 1 is a schematic show of the generation elongation (G-ELG) method. The blue circles are frozen units while the red circles are active units. As system is elongated, the active region (within the pink circle) can be approaching to the previously frozen units, leads to strong interaction between them. The G-ELG method recognizes this interaction and first re-activates those frozen units. After the elongation SCF converged, the CMOs will be re-localized so that the next elongation step will be continued without increasing the size of the interactive region. By repeating this procedure, any random with any-dimensional system can be generated by the G-ELG method.

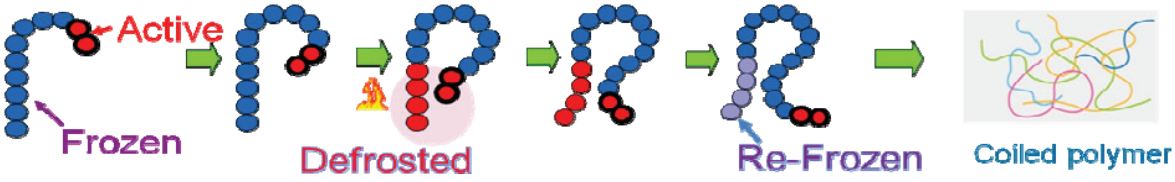
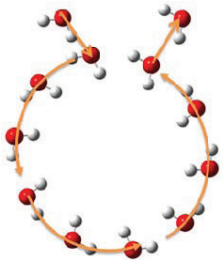
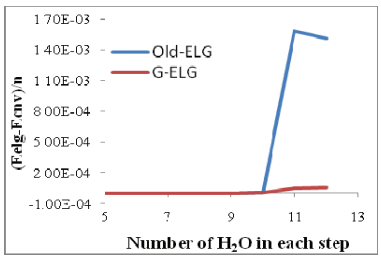


Fig. 1

Results and discussion:

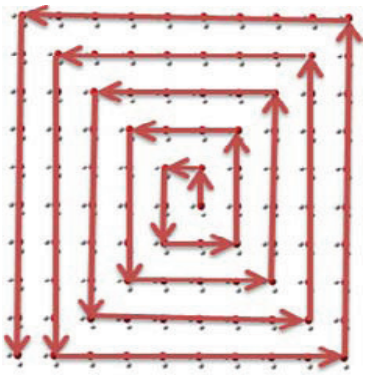
Fig. 2





One-dimensional water clusters $(H_2O)_{12}$ have been calculated by using the G-Elg, Old-Elg and conventional methods, as shown in Fig. 2. The procedures of the elongation method are described as the left side in Fig. 2. It can be seen from Fig. 2, because the strong interaction between the eleventh H_2O and the second H_2O, the energy difference calculated by the Old-Elg is abruptly increased when the eleventh water was involved. While for the G-Elg method, the energy difference is negligibly small because the second frozen water has been re-activated and included in the interactive space.

The two-dimensional water clusters have also been calculated by using the G-Elg method in this work, the total energy difference between the conventional and G-Elg calculations is shown in Fig. 3. In order to consider the strong interaction between the frozen region and the attacking monomer, any frozen units in 6 au, 10au, 15au and 20au around the attacking monomer will be re-activated, as shown in Fig. 3. As for different distances, the number of re-activated H_2O is given in Table 1. One can see from Fig. 3, with the increase of distance, the energy difference between the conventional and G-Elg calculations are decreased. Therefore, the G-Elg calculation can give the satisfactory results for two-dimensional system.



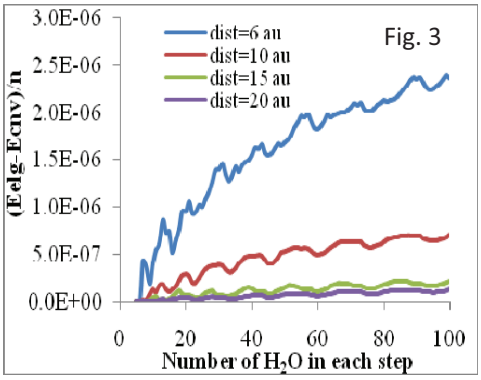
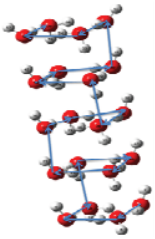


Fig. 3

Table 1

Distance (a.u.)	Number of re-activated H_2O
6	2
10	5
15	12

For the three-dimensional system, the stability energy (SE) of water cluster $(H2O)_{20}$ has also been calculated by using the G-Elg approach. The optimized geometry was taken from the work of Sathyamurthy et al (as shown in Fig. 4). Compared to the result of Sathyamurthy's, the stability energy calculated by the G-Elg method at HF/6-31G(d,p) level is in very good agreement (see Table 2).



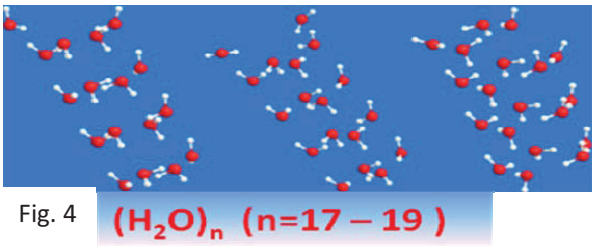


Fig. 4

Table 2 SE(kcal/mol)

Conv [11]	G-Elg*
-216.28 (HF)	-216.28 (HF)
-68.60 (MP2)	-65.72 (MP2)

In the present work, we showed the effectiveness and efficiency of the G-Elg method for the one-dimensional, two-dimensional, and three-dimensional water cluster models. The application of the G-Elg method to other large biological systems of interests, such as protein or DNA is in progress in our lab.

References:

[1] A. Imamura, Y. Aoki, and K. Maekawa, J. Chem. Phys., 95 (1991) 5419.
[2] Y. Aoki and A. Imamura, J. Chem. Phys., 97 (1992) 8432.
[3] F. L. Gu, Y. Aoki, J. Korchowiec, A. Imamura, and B. Kirtman, J. Chem. Phys., 121 (2004) 10385.
[4] "Elongation Method for Polymers and its Application to Nonlinear Optics, in Atoms, Molecules and Clusters in Electric Fields: Theoretical Approaches to the Calculation of Electric Polarizabilities", Feng Long Gu, Akira Imamura, and Yuriko Aoki, (edited by G. Maroulis, Imperial College Press), Vol. 1, Page 97-177, 2006.
[5] J. Korchowiec, F. L. Gu, A. Imamura, B. Kirtman, and Y. Aoki, Int. J. Quantum Chem., 102 (2005) 785.
[6] M. Makowski, J. Korchowiec, F. L. Gu, Y. Aoki, J. Comp. Chem., 27 (2006) 1603.
[7] Y. Orimoto, F. L. Gu, A. Imamura, and Y. Aoki, J. Chem. Phys., 126 (2007) 215104.
[8] S. Ohnishi, Y. Orimoto, F. L. Gu, and Y. Aoki, J. Chem. Phys., 127 (2007) 084702.
[9] F. L. Gu, Y. Aoki, A. Imamura, D. M. Bishop, and B. Kirtman, Mol. Phys. 101 (2003) 1487.
[10] S. Ohnishi, F. L. Gu, K. Naka, A. Imamura, B. Kirtman, and Y. Aoki, J. Phys. Chem. A, 108 (2004) 8478.
[11] S. Maheshwary, N. Patel, and N. Sathyamurthy *J. Phys. Chem*., A, 105 (2001) 10525.